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Processing of poly(lactic acid): Characterization of chemical structure, thermal stability and mechanical properties

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ABSTRACT

The processing of poly(lactic acid) (injection and extrusion/injection) as well as annealing of processed materials were studied in order to analyze the variation of its chemical structure, thermal degradation and mechanical properties. Processing of PLA was responsible for a decrease in molecular weight, as determined by GPC, due to chain scission. The degree of crystallinity was evaluated by means of differential scanning calorimetry and X-ray diffraction. It was found that mechanical processing led to the quasi disappearance of crystal structure whereas it was recovered after annealing. These findings were qualitatively corroborated by means of FTIR. By analyzing ^{1}H NMR and ^{13}C NMR chemical shifts and peak areas, it was possible to affirm that the chemical composition of PLA did not change after processing, but the proportion of methyl groups increased, thus indicating the presence of a different molecular environment. The thermal stability of the various materials was established by calculating various characteristic temperatures from thermograms as well as conversion and conversion derivative curves. Finally, the mechanical behaviour was determined by means of tensile testing (Young modulus, yield strength and elongation at break).

1. Introduction

Much attention has been paid to biodegradable polymers in recent years because of their wide range of applications in biomedical, packaging and agriculture fields [1]. The most popular biodegradable polymers are poly(lactic acid) (PLA), polycaprolactone (PCL), poly(butylene adipate terephthalate) (PBAT) and polyhydroxybutyrate (PHB) [2–6].

Poly(lactic acid) is a linear aliphatic thermoplastic polyester, produced from renewable resources and readily biodegradable, as an alternative to conventional polymers, such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS). Poly(lactic acid) is produced by ring-opening polymerization of lactide, and the lactic acid monomers are obtained from the fermentation of sugar feed stocks [7]. Fermentation of D-glucose from corn and other biomass substrates allowed the production of lactic acid at a price considerably cheaper than that previously achievable from petrochemical-derived products. Generally, commercial PLAs are copolymers of poly(L-lactic acid) (PLLA) and poly(D,L-lactic acid) (PDLA). The ratio of L- and D,L- enantiomers influences the properties of poly(lactic acid), such as melting temperature and crystallinity. Poly(lactic acid) can exhibit classical crystallization during both cooling and heating (the latter is metastable). This phenomenon probably depends on its molecular weight [8–10].

Poly(lactic acid) has numerous interesting properties including good mechanical properties, thermal stability, processability and low environmental impact. Polymer thermo-mechanical recycling has been studied and the general trend is a slight decrease of its mechanical properties after several injections or moulding processes. The major problem of recycling is the thermal stability, which has been reported as a complex process [11]. The presence of moisture (which causes hydrolysis), lactic acid residues and metal catalysts are known to favour PLA degradation.

The thermal degradation and stability of polymer materials have been studied by means of various techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA), FTIR spectroscopy and high-resolution pyrolysis-gas chromatography, among others [12,13]. These works analyzed the thermal degradation from different points-of-view: determination of activation energies,

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glass transition temperature, conversion, rate, thermal stability, enthalpy changes as well as identification of products.

It has to be noted that FTIR is a technique widely used to evaluate the conversion of functional groups present in polymer materials, thus leading to the quantification of various types of transformations within their chemical and physical structure, such as ageing of polymers, interactions in polymer composites, crystallinity, and cure of resins and composites [14–17].

PLA presents quite interesting properties if compared to commodity polymers [18,19], as shown in Table 1. It can be highlighted that PLA presents the highest mechanical properties, but the lowest thermal resistance. However, when the applications allows the use of PLA, this polymer presents some advantages like good processability in conventional industrial transformation equipments and biocompatibility [20,21].

Thermal degradation of PLA is very complex and various mechanisms have been postulated, including various non-radical and radical reactions: random chain scission reactions, depolymerization, oxidative degradation, intramolecular and intermolecular transesterifications, hydrolysis, pyrolytic elimination and radical reactions [22–33].

(i) Random chain scission reactions. Doi et al. (1990) [34] claimed that thermal degradation and hydrolysis of microbial polyesters occurred via random chain scission regardless of the type and the chemical composition by showing there was a linear relationship between the inverse of number-average degree of polymerization and time.
(ii) Intramolecular transesterification. The degradation of PLA during the melt is mainly caused by intramolecular transesterification reactions leading to cyclic oligomers of lactic acid and lactide. Simultaneously, there is a recombination of the cyclic oligomers with linear polyesters through insertion reactions, while molecules with longer chains lengths are favoured. According to Wachsen et al. [29,30], the degradation of PLA during thermal processing is mainly caused by intramolecular transesterification.
(iii) Intermolecular transesterification. It is the reaction between two ester molecules which exchange their radicals, thus leading to a variation of the distribution of molecular weights. Only a few works considered the intermolecular transesterification [35,36] as a mechanism present during the degradation in the melt, which can be minimized by the addition of benzoyl peroxide [37], 1,4-dianthraquinone [38] and other stabilizers.
(iv) Hydrolysis. The hydrolysis leads to the cleavage of the ester linkage, with the production of acid and alcohol groups. Ester splitting depends on the water content.
(v) Pyrolytic elimination. It leads to the formation of an acid and a molecule with acrylic end groups. This is a less important side reaction. The pyrolytic elimination results in species containing conjugated double bonds due to the carbonyl groups [32].
(vi) Radical degradation. This type of degradation needs only be taken into consideration at temperatures above 250 °C. These reactions can be assumed to start with either an alkyl-oxygen or an acyl-oxygen homolysis [27].

Moreover, reactive end groups, residual catalyst, unreacted starting monomer and impurities have been reported to enhance the PLA thermal degradation [26].

The aim of this study was to determine the chemical structure, crystallinity, thermal stability and mechanical properties of poly (lactic acid) after being processed by means of industrial thermoplastic processing methods (injection and extrusion followed by injection) with or without a further thermal treatment (i.e. annealing).

2. Materials and methods

2.1. Materials and processing

Poly(lactic acid) polymer 2002D, a product of Natureworks®, was kindly supplied by Nupik International (Polinyà, Spain). According to the manufacturer, this PLA has a D content of 4.25%, a residual monomer content of 0.3%, a relative density of 1.24, a glass transition temperature (T_g) of 58 °C and a melting point of 153 °C.

In this investigation, different processing configurations were studied. First, the raw PLA was injected in an MATEU&SOLÉ 7022 injection moulding machine, with a temperature profile of 180, 200 and 210 °C, and 210 °C for the nozzle. The injection pressure was kept constant at 100 bars and the mould temperature was fixed at 25 °C. Given that PLA is a polymer susceptible to hydrolysis [2], the pellets were dehumidified at 80 °C for 4 h under reduced pressure in a PIOVAN (DSN506HE) dryer (dew point = −40 °C). These conditions of temperature and time were optimized in order to reach moisture values near to zero. Indeed, dehumidification conditions were optimum because no hydrolysis reactions were present during the material processing, as confirmed by the absence of new hydroxyl groups (as determined by ^{1}H NMR and FTIR), from carboxylic acids and alcohols (which would be the products of ester hydrolysis). PLA was injected in an ISO normalized mould of specimens (prismatic bars with the following nominal dimensions: $6.35 \times 12.7 \times 127$ mm^3) for tensile testing. Afterwards, some of the injected pieces were

Table 1
Comparison of physical properties between PLA and commodity polymers.

	PLA	PS	i-PP	PET
Relative density	1.24	1.04–1.06	0.91	1.37
Clarity	Transparent	Transparent	Translucent	Transparent
MECHANICAL PROPERTIES				
Tensile yield strength (MPa)	48–110	34–46	21–37	47
Tensile modulus (GPa)	3.5–3.8	2.9–3.5	1.1–1.5	3.1
Tensile elongation (%)	2.5–100	3–4	20–800	50–300
Notched Izod impact, 23 °C (J/m)	13		72	79
THERMAL PROPERTIES				
Glass transition temperature (°C)	60	95	0	75
Melting temperature (°C)	153		163	250
Vicat temperature (°C)	55–60	84–106	80–140	74–200
Processing temperature (°C)	210	230	225	255